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Determination of sarin, soman and their hydrolysis products in soil by packed capillary liquid chromatography–electrospray mass spectrometry

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Abstract

An analytical method based on aqueous ultrasonic extraction and packed capillary liquid chromatography–electrospray mass spectrometry (LC–ESI–MS) analysis was developed and compared to an existing gas chromatography(GC)–MS based method for the determination of sarin, soman and their hydrolysis products in contaminated soil. Three soils, a red clay, a tan sandy clay and a brown sandy clay loam, were spiked with sarin and soman and their initial hydrolysis products, isopropyl methylphosphonic acid and pinacolyl methylphosphonic acid, at the 10 μg/g level to assess recovery efficiency. Recovery of sarin and soman from the aqueous soil extracts was comparable to the existing analytical method, with a significant improvement in recovery being demonstrated for the chemical warfare agent hydrolysis products. Sarin and soman were recovered in the 20–90% range from the three soil types with aqueous extraction, while the hydrolysis products of these chemical warfare agents were extracted with recoveries in excess of 80%. The developed soil extraction and analysis method appears to be an attractive alternative to the GC–MS based method, since aqueous extracts containing chemical warfare agent hydrolysis products may be analysed directly, eliminating the need for additional sample handling and derivatization steps. Crown copyright © 2001 Published by Elsevier Science B.V. All rights reserved.

Keywords. Soil; Chemical warfare agents, Sarin; Soman, Organophosphorus compounds

1. Introduction

Peacekeeping units routinely participate in operations in regions of the world where exposure to chemical warfare agents may occur. Under these circumstances, collection of representative samples would typically take place to confirm the identity of the chemical(s). Analyses of these types of samples require the use of sensitive, specific analytical methods, since unambiguous proof is required to substantiate the prior presence of chemical warfare agents [1]. Recently, a Canadian sampling team was sent to Eastern Europe to collect sandbag and soil samples from a site for chemical warfare agent analysis by the Defence Research Establishment Suffield. Chemical warfare agents were not detected in any of the soil extracts, but the different soils types were utilized for the development of a new analytical method for soil analysis.

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Gas chromatography (GC) has been used extensively for the separation and identification of the chemical warfare agents, with gas chromatography–mass spectrometry (GC–MS) being used most frequently for the characterization of these compounds [1,2]. Organophosphorus chemical warfare agents have been studied extensively by electron impact and chemical ionization mass spectrometry, as the use of these complementary ionization techniques facilitates the acquisition of molecular and fragmentation ion information that may be used for identification [3–5]. GC separation, while suitable for the direct analysis of organophosphorus chemical warfare agents in organic extracts, is usually not preferred for the direct analysis of aqueous samples or extracts. Aqueous samples or extracts containing organophosphorus chemical warfare agents and/or their nonvolatile hydrolysis products normally require additional sample handling steps and derivatization [6–8]. Water samples containing chemical warfare agents have been analysed by GC–MS following solid-phase microextraction [9], by capillary electrophoresis [10–13] and by microcolumn liquid chromatography (LC) with flame photometric detection [14]. Increasingly, researchers have developed LC–MS analytical methods to deal with the analysis of aqueous samples containing these nonvolatile hydrolysis products [15–21].

Thermospray mass spectrometry [15–18] and more recently the atmospheric pressure ionization (e.g., electrospray (ESI), ionspray and atmospheric pressure CI) techniques [19–26] have been employed for the analysis of organophosphorus chemical warfare agent hydrolysis products. Each technique may be interfaced to LC for component separation, with thermospray–MS having been largely superseded by atmospheric pressure ionization (API) for LC–MS analyses. Most ESI–MS applications deal with the analysis of higher molecular mass compounds, such as peptides or proteins, and only recently has ESI–MS been applied to analysis of chemical warfare agents in aqueous samples [27,28].

An existing analytical scheme involving organic solvent extraction and trimethylsilylation has been used for the determination of chemical warfare agent and their hydrolysis products in a variety of soils [7]. The analytical method was evaluated with four different soils spiked at the 50 and 5 μg/g level with sarin, soman, mustard and the chemical warfare agent simulant, triethyl phosphate. These spiking levels were well below typical battlefield contamination levels, estimated to be in the 100–1000 μg/g range, based on a contamination density of 1 to 10 g/m^2 (soil density about 1 g/cm^3 and a 1 cm sampling depth). The 50 μg/g level was considered typical of soil contamination levels that might be expected hours to days after an attack, while lower levels would be typical of soil samples that had undergone weathering. Organophosphorus chemical warfare agents and triethyl phosphate were extracted most efficiently with dichloromethane with recoveries from the soils generally in the 5–70% range [7]. Each spiked soil sample was also trimethylsilylated in an effort to determine the presence of chemical warfare agent hydrolysis products. Hydrolysis products were detected but recovery efficiencies were not estimated.

LC–ESI–MS has been used for the direct determination of chemical warfare agents, their hydrolysis products and related compounds in aqueous samples during a single analysis [27,28]. This approach was an attractive alternative to GC–MS for these analyses, as both the organophosphorus chemical warfare agents and/or their hydrolysis products could be analysed directly without the need for additional sample handling and derivatization. A similar analytical advantage might be realized for the analysis of aqueous extracts of chemical warfare agent contaminated soil samples.

This paper focuses on the development of an aqueous extraction scheme for contaminated soil samples and the analysis of these extracts by packed capillary LC–ESI–MS. Three Eastern European soil types, a red clay, a tan sandy clay and a brown sandy clay loam, were selected and spiked with sarin, soman and/or their initial hydrolysis products, isopropyl methylphosphonic acid and pinacolyl methylphosphonic acid, at the 10 μg/g level to assess the potential of an aqueous extraction method for soil analysis. Mass spectrometric characterization and quantitation were performed by packed capillary LC–ESI–MS with a time-of-flight (TOF) instrument. Recovery of sarin and soman from the aqueous soil extracts was comparable to the existing dichlorome-

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thane extraction method [7], with a significant improvement in recovery being demonstrated for the chemical warfare agent hydrolysis products.

2. Experimental

2.1. Samples

The Eastern European soil samples were of three general types and representative samples of each were selected for the development and evaluation of an aqueous extraction and analysis method. The soils were a red clay, a tan sandy clay and a brown sandy clay loam. Each of the soils (1 g) was spiked in triplicate at the 10 μg/g level using 10 μl of a 1 mg/ml standard containing chemical warfare agents and/or chemical warfare agent hydrolysis products (in dichloromethane). The exception was the 50 μg/g spike of the soils to evaluate recovery of chemical warfare agent hydrolysis products using an existing clean-up scheme [7]. Each spiked soil sample was extracted after standing 1 h at 4°C using either the existing clean-up scheme (GC–MS based method) or the developed aqueous clean-up scheme (LC–ESI–MS based method).

Chemical warfare agents, their hydrolysis products and triethyl phosphate were provided by the Canadian National Single Small Scale Facility at DRES.

2.2. Existing clean-up and analysis method (GC–MS based method)

Soil samples and spiked soil samples were handled in a manner similar to a published method [7]. One gram of each soil sample was weighted and transferred into 16×125 mm glass culture tubes. Each soil sample was extracted with 3 ml of dichloromethane by ultrasonic vibration (10 min) and then centrifuged at 700 *g* for 10 min. The dichloromethane layer (1.5 ml) was removed and concentrated under a gentle stream of helium to 75 μl. One microlitre injection(s) were used for GC–MS determination of chemical warfare agents in each soil extract.

Trimethylsilylation was used to enhance the volatility of any chemical warfare agent hydrolysis products that may be associated with the soil samples. 100 μl of bis(trimethylsilyl)-trifluoroacetamide (BSTFA) and 100 μl pyridine were added to the remaining soil and dichloromethane (approximately 1.5 ml) in each culture tube. The contents were vortexed and the tube was placed in an ultrasonic bath for 10 min. The soil samples were then heated for 20 min at 60°C and centrifuged for 10 min at 700 *g*. A portion of the trimethylsilyl/dichloromethane layer (0.5 ml) was removed and 1 μl aliquots were used during GC–MS analysis for the presence of chemical warfare agent hydrolysis products.

Capillary column gas chromatographic–mass spectrometric (GC–MS) analyses were performed with a Trio-1 bench-top instrument under electron impact (EI) operating conditions (emission, 0.15 mA; electron energy, 70 eV and source temperature, 200°C). Full scanning MS data were acquired with unit resolution (50% valley definition) at 1 s/scan over a 40–400 u mass range. GC separations were performed with a HP 5890 gas chromatograph equipped with an on-column injector. A 15 m×0.32 mm I.D. DB-1701 J&W capillary column (film thickness: 0.25 μm) was used for all GC–MS analyses with the following temperature program: 40°C (2 min) 10°C/min 280°C. A 1-min solvent delay was used prior to MS data acquisition of the dichloromethane extracts. A longer solvent delay, 6 min, was required for the trimethylsilyl/dichloromethane extracts to minimize MS data acquisition of the numerous solvent/derivatizing reagent components. Quantitation were performed with a HP 5890 gas chromatograph equipped with a flame ion ionization detector under similar chromatographic conditions using a 15 m×0.53 mm I.D. DB-1701 J&W capillary column (film thickness: 1 μm).

2.3 Aqueous clean-up and analysis method (LC–ESI–MS based method)

One gram of each soil sample was weighted and transferred into 16×125 mm glass culture tubes. Each soil sample and spiked soil sample was extracted with 1 ml of water by ultrasonic vibration (10

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min) and then centrifuged at 700 *g* for 10 min. A portion of the water layer was removed (200 μl) and 5 μl injection(s) were used for LC–ESI–MS determination of chemical warfare agents and/or their hydrolysis products.

ESI–MS data were acquired using a Micromass LCT time-of-flight mass spectrometer equipped with the Z-spray electrospray interface. The electrospray capillary was operated at 3.2 kV and the sampling cone voltage was either 20 or 30 V. Nitrogen desolvation gas was introduced into the interface (80°C) at a flow-rate of 480 l/h. Nitrogen nebulizer gas was introduced at a flow-rate of 66 l/h. ESI–MS data were acquired from 1000 to 70 Da (1 s) in the continuum mode with a resolution of 5000 (50% valley definition).

LC separations were performed using an Applied Biosystems Model 140B dual syringe pump equipped with a Micro-Tech (Sunnyvale, CA) 150× 0.32 mm I.D. Zorbax C_{18} SB (5 μm) packed fused-silica capillary column and a Rheodyne 8125 injector with a 5 μl sample loop. The following solvent compositions were prepared for LC separation: Solvent A (0.1% trifluoroacetic acid in water) and Solvent B (0.1% trifluoroacetic acid in acetonitrile (ACN)/water, 95 5). Chromatographic separations were performed using a 1 to 75% B gradient program over 30 min. In order to minimize dead volume effects and ensure reproducible mixing, the mobile phase was delivered at 200 μl/min and split prior to the injector such that the flow through the column was 16 μl/min.

3. Results and discussion

The GC–MS based method [7] used for the analysis of Eastern European soil samples utilizes dichloromethane ultrasonification for the extraction of chemical warfare agents from contaminated soils. Extraction efficiency will vary with soil type, but in-house experience has shown that most chemical warfare agents will be extracted with sufficient efficiency to enable identification. The efficiency of chemical warfare agent hydrolysis product extraction as their trimethylsilyl derivatives was not evaluated, as the focus in the earlier paper was on the qualitative observation of residual hydrolysis products resulting from hydrolysis of the spiked chemical warfare agents. With the introduction of commercial LC–ESI–MS systems, analytical methods that make use of reverse phase columns and acetonitrile or methanol/water mobile phases could be developed for the analysis of aqueous extracts or samples. Given the polarity and solubility of the chemical warfare agent hydrolysis products in water, a method utilizing aqueous ultrasonic extraction and reversed-phase LC–ESI–MS analysis seemed worth investigating. If applicable, this approach would allow for the direct analysis of aqueous extracts without the need for additional sample handling and derivatization. It would also eliminate the concern over the presence of moisture in soil samples, a factor that impedes the derivatization process required for GC–MS analyses.

Three representative soils, a red clay, a tan sandy clay and a brown sandy clay loam were selected for the development, evaluation and comparison of an aqueous based extraction and analysis scheme with the existing method. The existing clean-up scheme was evaluated by spiking the soil samples at the 10 μg/g level with sarin, soman, mustard and triethyl phosphate or at the 50 μg/g level with isopropyl methylphosphonic acid, pinacolyl methylphosphonic acid and thiodiglycol. The extraction efficiency of each spiked compound was determined for each soil in triplicate (at a minimum) by capillary column GC–flame ionisation detection (FID).

The same soil samples were also spiked with sarin, soman and their initial hydrolysis products, isopropyl methylphosphonic acid and pinacolyl methylphosphonic acid, at the 10 μg/g level. Each sample was extracted with water using the developed method and analysed in triplicate by packed capillary LC–ESI–MS. Soil samples were also spiked with just the hydrolysis products, since hydrolysis of the spiked organophosphorus chemical warfare agents during sample extraction or standing was anticipated. Mustard was not used during spiking experiments since, unlike organophosphorus chemical warfare agents and their hydrolysis products [27,28], it does not appear to ionize during ESI–MS

Table 1 summarizes the dichloromethane extrac-

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Table 1
Recovery of sarin, soman, triethyl phosphate and mustard from three soil samples spiked at the 10 μg/g level (dichloromethane extract)*

Soil sample	Percent recovery (mean±SD)			
	Sarin	Soman	Triethyl phosphate	Mustard
Red clay	22±3 (n=5)	61±10 (n=5)	86±8 (n=5)	81±14 (n=5)
Tan sandy clay	63±8 (n=5)	80±5 (n=5)	93±5 (n=5)	53±5 (n=5)
Brown sandy clay loam	27±4 (n=3)	62±3 (n=3)	75±3 (n=3)	80±2 (n=3)

* Recovery determined by capillary column GC–FID

tion efficiencies for the chemical warfare agents spiked at the 10 μg/g level using the existing GC–MS based method. All the spiked chemical warfare agents and the simulant, triethyl phosphate, were recovered from the soil samples with efficiencies that would be more than sufficient for retrospective confirmation purposes. Recovery of soman, mustard and triethyl phosphate was determined by capillary column GC–FID (Fig. 1) and exceeded 50% for all three soil types. Sarin was recovered efficiently from the tan sandy clay (approximately 60%) but was only recovered in the 20–30% range from the other two

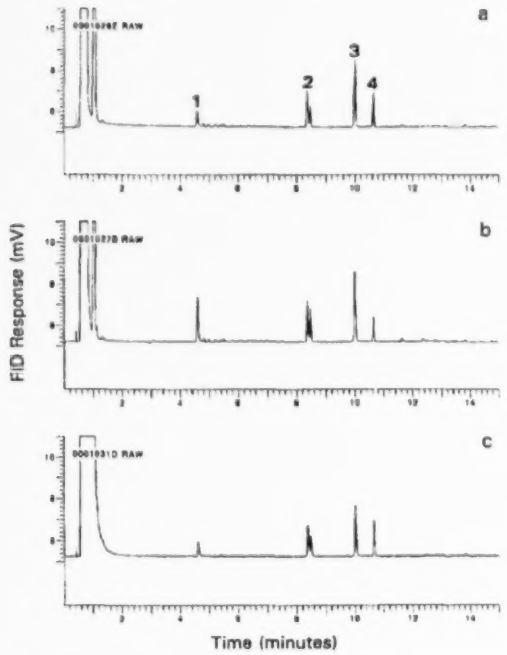

Fig 1 Capillary column GC–FID chromatograms obtained for dichloromethane extract of (a) red clay, (b) tan sandy clay and (c) brown sandy clay loam soil samples spiked at the 10 μg/g level with sarin (1), soman (2), triethyl phosphate (3) and mustard (4)

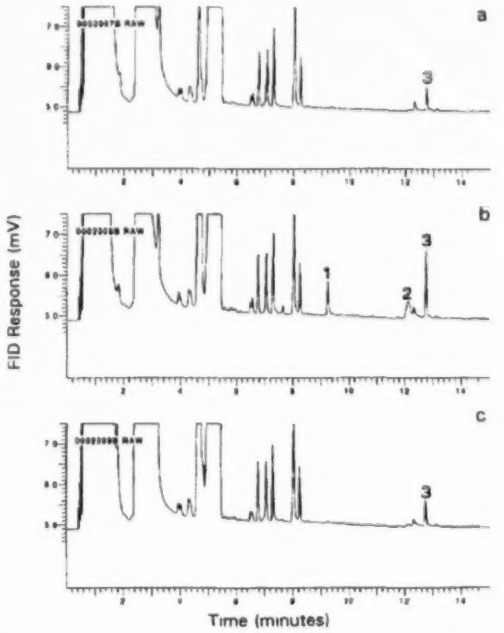

Fig 2 Capillary column GC–FID chromatograms obtained for trimethylsilyl/dichloromethane extract of (a) red clay, (b) tan sandy clay and (c) brown sandy clay loam soil samples spiked at the 50 μg/g level with isopropyl methylphosphonic acid (1), pinacolyl methylphosphonic acid (2) and thiodiglycol (3).

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Table 2
Recovery of isopropyl methylphosphonic acid (iPrMPA) pinacolyl methylphosphonic acid (PinMPA) and thiodiglycol from three soil samples spiked at the 50 μg/g level (trimethylsilyl/dichloromethane extract)[a]

Soil sample	Percent recovery (mean±SD)		
	iPrMPA	PinMPA	Thiodiglycol
Red clay	Not detected	Not detected	10±1 (n=3)
Tan sandy clay	36±9 (n=3)	34±2 (n=3)	53±5 (n=3)
Brown sandy clay loam	Not detected	Not detected	11±2 (n=3)

[a] Recovery determined by capillary column GC–FID

soil types. These recoveries were compared to the recovery of the same compounds in the prior study and were found to be slightly higher [7].

Three chemical warfare agent hydrolysis products, isopropyl methylphosphonic acid, pinacolyl methylphosphonic acid and thiodiglycol, were spiked onto each of the three soil types at a higher level than the chemical warfare agents, 50 μg/g, since there were significant chemical interferences associated with the derivatization procedure (numerous chromatographic peaks between 0 and 8 min in Fig. 2). Table 2 summarizes the recovery efficiencies for each hydrolysis product and Fig. 2 illustrates typical capillary column GC–FID chromatograms used for quantitative purposes. All three hydrolysis products were only recovered from the tan sandy clay soil (recovery efficiency in the 30–60% range). Only thiodiglycol was recovered from the remaining two soil types. Method improvement or development of a new method would be required to reliably detect and confirm the chemical warfare agent hydrolysis products in these soil types.

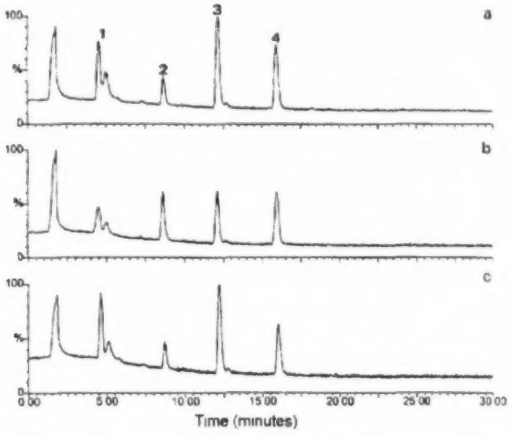

Fig. 3. Packed capillary LC–ESI–MS total ion current (m/z 400 to m/z 85) chromatograms obtained for an aqueous extract of (a) red clay, (b) tan sandy clay and (c) brown sandy clay loam soil samples spiked at the 10 μg/g level with isopropyl methylphosphonic acid (1), sarin (2), pinacolyl methylphosphonic acid (3) and soman (4).

Extraction of both the organophosphorus chemical warfare agents and their hydrolysis products with water from soil would be an attractive alternative as the aqueous extracts could be analysed directly by packed capillary LC–ESI–MS. This approach was initially investigated by extracting each of the soil samples with water, to provide an indication as to what other chemical(s) would be co-extracted. The chromatograms for all three soils were similar in that they contained a major component(s) eluting in the first few minutes of each chomatogram (Fig. 3). The mass spectrum obtained for the broad chromatographic peak was similar in ion content for all three soil sample extracts, although the relative intensities of the ions varied somewhat. No attempt was made to identify these component(s).

All three soil types were then spiked at the 10 μg/g level with sarin, soman, isopropyl methylphosphonic acid and pinacolyl methylphosphonic acid. Recovery data for sarin and soman were remarkably similar to the data obtained for their extraction with dichloromethane (Table 3), with the poorest extraction efficiency being for sarin from the red clay and brown sandy clay loam soil types. Fig. 3 illustrates typical packed capillary LC–ESI–MS total ion current chromatograms obtained for aqueous extracts of each of the spiked soil samples.

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Table 3
Recovery of sarin, soman, isopropyl methylphosphonic acid (iPrMPA) and pinacolyl methylphosphonic acid (PinMPA) from three soil samples spiked at the 10 μg/g level (aqueous extract) Recovery was determined by packed capillary LC–ESI–MS

Soil sample	Percent recovery (mean±SD)			
	Sarin	Soman	iPrMPA	PinMPA
Red clay	19±9 (n=3)	57±12 (n=3)	160±17 (n=3)[a] 80[b]	136±12 (n=3)[a] 87[b]
Tan sandy clay	77±11 (n=3)	86±10 (n=3)	124±7 (n=3)[a] 98[b]	116±17 (n=3)[a] 104[b]
Brown sandy clay loam	27±4 (n=3)	52±6 (n=3)	171±11 (n=3)[a] 101[b]	145±12 (n=3)[a] 110[b]

[a] Recoveries of isopropyl methylphosphonic acid (iPrMPA) and pinacolyl methylphosphonic acid (PinMPA) greater than 100% due to hydrolysis of sarin and soman, respectively
[b] Single spiking experiment using only iPrMPA and PinMPA

A large chromatographic peak was observed in the first few minutes of each chromatogram, consistent with the initial aqueous extract of the each soil sample. All four spiked compounds were readily detected and identified based on their acquired ESI–MS data (Fig. 4). The electrospray mass spectra of sarin and soman were similar to recently published data with both chemical warfare agents exhibiting $(M+H)^+$ (at m/z 141 for sarin and at m/z 183 for soman), $(M+H+ACN)^+$ ions (at m/z 182 for sarin and at m/z 224 for soman) and/or protonated dimers that could be used to confirm molecular mass. Product ions resulting from alkene loss from the alkoxy substituents (and their acetonitrile adducts) at m/z 99 were also observed for both sarin and soman [28]. Similar information was also evident in the electrospray mass spectra obtained for the two hydrolysis products, with both compounds exhibiting ions at m/z 97 due to alkene loss from the alkoxy substituents. The only anomaly noted during the analysis was the detection of two chromatographic peaks with identical mass spectra for isopropyl methylphosphonic acid. Peak splitting caused by the co-extracted soil sample components was suspected since analysis of the isopropyl methylphosphonic acid standard used for spiking experiments exhibited a single peak during LC–ESI–MS analysis.

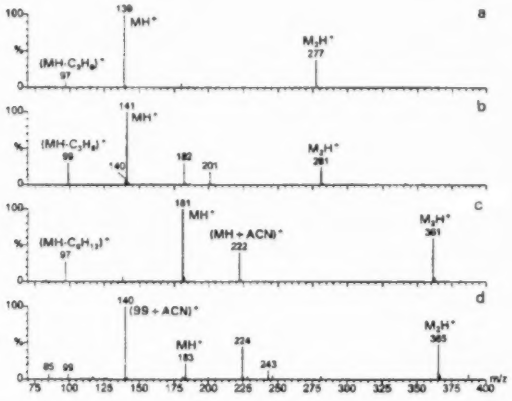

Fig 4 Typical ESI–MS data (sampling cone voltage 20 V) obtained for (a) isopropyl methylphosphonic acid, (b) sarin, (c) pinacolyl methylphosphonic acid and (d) soman during analysis of aqueous soil extracts

The recovery of hydrolysis products was almost quantitative with recoveries in excess of 80% for all three soil types (Table 3). In all cases the sum of the chemical warfare agent and hydrolysis product percentages accounted for nearly all the compound(s) spiked. Recovery percentages for both hydrolysis products exceeded 100% in Table 3 due to hydrolysis of a portion of the sarin and soman during sample standing and/or handling. This was verified during a single spiking experiment using only the two hydrolysis products (Table 3). Isopropyl methylphosphonic acid and pinacolyl methylphosphonic acid were recovered from the soils with efficiencies ranging from 80 to 101%, and 87 to 110%, respec-

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tively. These recoveries were much better than those found using the existing derivatization procedure and use of this new clean-up scheme would be recommended for the verification of chemical warfare agent hydrolysis products in contaminated soil samples, provided mustard was not suspected. Mustard was not detected by ESI–MS, although thiodiglycol and the many hydrolysis products of munitions grade mustard may be identified using this approach [26].

4. Conclusions

An analytical method based on aqueous extraction and packed capillary LC–ESI–MS analysis was developed for the determination of trace levels of sarin and soman and their hydrolysis products in contaminated soil samples. Three different Eastern European soils, a red clay, a tan sandy clay and a brown sandy clay loam, were selected and spiked with sarin and soman and their hydrolysis products, isopropyl methylphosphonic acid and pinacolyl methylphosphonic acid, at the 10 μg/g level to assess the efficiency of the aqueous extraction method for contaminated soil analysis. LC–ESI–MS characterization and quantitation was performed with a time-of-flight (TOF) instrument capable of acquiring continuum data on picogram quantities of analyte. Full mass spectra were acquired for each compound, with all spiked compounds exhibiting $(M+H)^+$, $(M+H+ACN)^+$ ions and/or protonated dimers that could be used to confirm molecular mass and product ions resulting from alkene loss from the alkoxy substituents (and their acetonitrile adducts).

Recovery of sarin and soman from the aqueous soil extracts was comparable to the existing dichloromethane extraction method. However a significant improvement in recovery was demonstrated for the recovery of chemical warfare agent hydrolysis products from the same soil samples. Sarin and soman were recovered in the 20–90% range from the three soil types with the aqueous extraction clean-up scheme, while their hydrolysis products were extracted almost quantitatively, with recoveries in excess of 80% for all three soil types. The developed aqueous extraction and LC–ESI–MS analysis method appears to complement the existing GC–MS based method, particularly when organophosphorus chemical warfare agent hydrolysis products require determination. Aqueous extracts of soil samples contaminated with organophosphorus chemical warfare agents and/or their hydrolysis products may be analysed directly during a single analysis, without the additional sample handling and derivatization required by the GC–MS based method.

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